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Survey of Safety Related Additives for Methanol Fuel

Southwest Research Inst., San Antonio, TX

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FOREWORD

This project Work Assignment was conducted for the U.S. Environmental Protection Agency, 2565 Plymouth Road, Ann Arbor, Michigan, 48105, by the Department of Emissions Research of Southwest Research Institute, 6220 Culebra Road, San Antonio, Texas, 78284. This project, authorized by Contract 68-03-3162, Work Assignment 5, was initiated on July 18, 1983 and completed February 18, 1984. The EPA Project Officer was Mr. Robert J. Garbe and the EPA Task Technical Officer was Mr. Thomas M. Baines, both of the Emission Control Technology Division, Environmental Protection Agency. The SwRI Project Leader was Dr. Lawrence R. Smith and the principal researcher at SwRI was Mr. E. Robert Fanick. The SwRI Project Manager was Mr. Charles T. Hare. This project was identified within Southwest Research Institute as (initially) 05-7338-005 and (later) 03-7338-005.

ABSTRACT

This report describes the effort to determine what additives may be feasible for use with 100% methanol motor vehicle fuel to increase the safety associated with the use of methanol as a motor vehicle fuel. A survey of the literature was conducted to determine candidate additives that would 1) ensure methanol burns with a visible flame, 2) prevent improper use of the fuel as a degreaser or cleaning agent, 3) give the fuel an unpleasant taste causing expectoration of any methanol accidentally in one's mouth, and 4) act as an emetic. Candidate additives were evaluated as to effectiveness, cost, ease of production, health problems associated with the additive, and estimated effects on vehicle performance.

TABLE OF CONTENTS

		Page
FOREWORD		iii
ABSTRACT		iv
LIST OF FIGURES		vi
LIST OF TABLES		vii
I.	SUMMARY	1
II.	FLAME LUMINOSITY	3
	A. Literature Search	3
	B. Evaluation	15
III.	TASTE DETERRENTS	18
	A. Literature Search	18
	B. Evaluation	26
IV.	DYES AND COLORANTS	29
	A. Literature Search	29
	B. Evaluation	33
V.	EMETIC	34
	A. Literature Search	34
	B. Evaluation	34
VI.	ODORANTS	37
	A. Literature Search	37
	B. Evaluation	42
VII.	OTHER METHODS TO INCREASE SAFETY	44
REFERENCES		47
APPENDIX		
	A. BACKGROUND AND HISTORY	

LIST OF FIGURES

Figure		Page
1	Experimental Rate of Absorption for Methanol Versus Time	30
2	Warning Sign for Storage Tanks and Containers	45
3	Warning Sign for Areas in Which Methyl Alcohol is Present	45

LIST OF TABLES

Table		Page
1	Potential Flame Luminosity Enhancers	5
2	Relative Radiation Characteristics of a Variety of Pure Hydrocarbons	4
3	Time Dependent Flame Luminosity with Methanol	7
4	Azeotrope Systems with Methanol	11
5	Effect of Water on Luminosity of Dimethylether-Primed Methanol	13
6	U.S. Government-Authorized Denaturants for Completely Denatured Alcohol (C.D.A.) and Specially Denatured Alcohol (S.D.A.)	19
7	Denaturant Formulas for Ethanol and Other Fuels	20
8	Compounds for Foul Taste	24
9	Current Costs of Several Widely used Taste Deterrents	27
10	Methanol Absorption Rate through the Skin at Different Exposure Times	31
11	General Automotive Fluid Colors	32
12	Therapeutic Category - Emetic	35
13	Odorant Tests: Odor of Various Odorants Above a Solution in Methanol	38
14	Odorant Tests: Evaporation of a Solution in Methanol into a Closed Room	39
15	Malodorous Substances	40

I. SUMMARY

The objective of this program was to evaluate additives which may be feasible for use with 100% methanol motor vehicle fuel to increase the safety associated with the use of the methanol fuel. These additives were evaluated regarding their ability to 1) ensure that methanol burns with a visible flame, 2) discourage improper use of the fuel as a degreaser or cleaning agent, 3) give the fuel an unpleasant taste causing expectoration of any methanol accidentally taken into the month, and 4) act as an emetic. The effectiveness, cost, ease of production, health problems associated with use, and estimated effects on vehicle performance were taken into account when evaluating the additives. Information for the study was obtained from a survey of the literature and from contact with numerous individuals having experience related to methanol, fuels in general, specified types of additives, and health and safety.

The scope of this study did not encompass the question of whether or not a given methanol fuel safety aspect should be addressed by use of fuel additives. Rather, the study departed from the position that the methanol fuel safety aspect should in fact be addressed by additives. Thus, this study was limited to issues such as additive effectiveness, cost, east of production, etc.

Due to methanol's low odor intensity, harmful levels of methanol vapor could go undetected. For this reason, the use of odorants as additives to methanol was also investigated. Additional safety measures, not related to the use of additives, were suggested in the literature and by several researchers. These additional measures are discussed briefly in Section VI of the report. A substantial amount of background information on methanol was also assembled during the course of the study, and this information has been summarized in an appendix for use as required.

The observations and conclusions that were reached in this study are listed below. The conclusions are based on information obtained from the literature and elsewhere.

1. For flame luminosity enhancement, the most practical and effective additives appear to be highly complex mixtures of hydrocarbons such as a reformate fraction distilling in the range of 55 to 220 C (4 volume percent addition) or unleaded gasoline (10 to 15 volume percent addition). These additives increase the cost of methanol fuel on the order of 10 to 15 percent, however, a large portion of this would be offset by the higher energy content of the hydrocarbon mixtures. These mixtures form a number of azeotropes with methanol which burn with a visible flame that persists throughout the duration of combustion of the mixtures fire. The addition of complex mixtures of hydrocarbons, such as unleaded gasoline, also aids in other related areas such as reducing the flammability of the methanol vapor in a closed system (i.e., fuel tank), increasing the ability to start an engine at low ambient temperatures, and increasing the odor and taste intensity of the fuel blend.

2. For taste deterrence, two additives appear viable. Gasoline (or other complex mixtures of hydrocarbons) also appears to be a reasonable additive to methanol as a taste deterrent. Gasoline can not be removed easily from a mixture with methanol, and researchers have reported that even a determined consumer would have difficulty in swallowing such a mixture. Bitrex (a taste deterrent used in paints, detergents, and other products) is one of the most bitter substances known to man and would also be a prime candidate as a taste deterrent for methanol. If used in methanol at concentrations similar to those used in other applications (2-9 ppm), Bitrex would be relatively inexpensive (0.5 to 2.1 cents per gallon of methanol) and effective taste deterrent.

3. Dyes appear to be the best way to discourage the use of methanol as a degreasing or cleaning agent. A number of dyes in a variety of colors are soluble in methanol. Commercial methanol products have typically been blue in color, and a continuation of this practice would be logical for fuel methanol. A concentration of only 4 milligrams of dye per gallons of methanol (at a cost of 0.02 cents/gallons methanol) has been found to give an easily recognizable color. A concentration of 400 milligrams per gallon, however, was needed to stain the skin. This concentration of dye would cost about 2 cents per gallon of methanol. However the desirability of the use of such large concentrations of dyes would have to be investigated, as a methanol fuel containing a sufficient dye to stain the skin could result in irreversible coloration of clothing and vehicle components, could cause excess engine wear due to deposits, and could lead to additional exposures to toxic cleaning compounds when trying to remove the dye from skin or clothing.

4. The use of an emetic as an additive for methanol was evaluated to determine if its use would be practical to induce vomiting if the methanol fuel was consumed. This appears impractical, however, as the necessary concentration of an emetic (such as ipecac) in methanol required to induce vomiting was found to be about eight volume percent. The cost for such a quantity of ipecac would be $85/gallon of methanol and its use would drastically reduce the availability of emetics for established applications. The use of a large quantity of an emetic in fuel could also cause engine damage if the selected emetic differs greatly in composition from the fuel.

5. Due to methanol's low odor intensity, added odorants are necessary to enhance olfactory detection of methanol vapors. Mercaptans have been shown to be effective odorants for methanol at concentrations as low as 200 mg per gallon methanol. Mercaptans are used in natural gas, so their use in methanol could cause some confusion (i.e., is it a methanol spill or natural gas leak) when their odor is detected. The more chemically stable organic sulfides, which have a slightly different but equally intense odor, may be more desirable.

II. FLAME LUMINOSITY

One of the chemical properties of neat methanol is that pools of liquid methanol burn with a low luminosity, bluish flame which is essentially invisible especially in daylight. Methanol flame radiation occurs primarily at infrared wavelengths that are invisible to the naked eye. The property of low flame luminosity is not desirable because an invisible fire is difficult to detect and thus more difficult to extinguish. A visible flame increases the safety factor, since one could adequately detect any accidental fires and move to safety or take steps to extinguish the flame.

A. Literature Search

The luminosity of a burning substance is in part related to the formation of submicroscopic soot particles during the combustion process. These carbonaceous particles are heated by the flame and subsequently emit "grey-body" radiation at visible light wavelengths. Methanol is unusual because it burns with a cooler flame, and its combustion produces no carbonaceous particles. Since no "grey-body" radiation occurs with methanol, the flame radiates at infrared wavelengths derived from the heated gaseous combustion products. Neat methanol has one of the lowest radiation characteristics during combustion compared to other hydrocarbon materials. The addition of hydrocarbons is one means of enhancing the luminosity of methanol in a flame by increasing the tendency to produce "grey-body" radiation.

Methanol has been used in racing fuels for more than 40 years. It is used as the base fuel and blended with other substances in drag racing applications or neat in "Indianapolis car" applications. Other racing applications, including Formula I, CAN-AM, stock, sports and production cars, use a conventional gasoline fuel with octane boosters. The National Hot Rod Association (NHRA), the International Hot Rod Association (IHRA) and the American Hot Rod Association (AHRA) do not have fuel specifications,[1] with the exception that hydrazine and compressed gases (i.e., nitrous oxide) are to be used only in Top Fuel and AA/Funny Car Classifications.[2] In the "alcohol only" racing classifications, no additives are introduced specifically to increase flame luminosity or for other safety purposes. A color indicator dye, however, is used in nitromethane to indicate the presence of hydrazine. The substances that are added to drag racing fuels are for the purpose of increasing power rather than flame luminosity. Some of these additives do enhance the flame luminosity, although many of them could not be used for street vehicle applications. At least one fuel supplier, Lindele Corp., advertises a methanol fuel, "Racing Blue," which is said to burn with a red/orange flame for increased flame luminosity however, the contents of the additive package were not disclosed. Lindele Corp. company also produces a red-dyed methanol fuel that is designed for street vehicle use.

The Champion Auto Racing Team (CART) and the United States Auto Club (USAC), which run the Indianapolis cars, specify neat methanol as the fuel.[3] Prior to 1973, the fuel supplied to the racers was free, and any blend could be used. From 1973 until the present, methanol was specified because it is readily available, uniform in composition, easily identified and controlled,

and reasonable in cost. CART and USAC have investigated a few additives for flame luminosity enhancement, but to date no data have been published. Flame luminosity is not considered a necessarily desirable property for racing applications. Instead, safety precautions and education are considered more desirable and effective. Ground wires for the vehicles, dry break systems (a fuel tank to fuel filler nozzle connection that, upon uncoupling, shuts off the fuel flow) with gravity fill for fueling, fire proof uniforms, anodized aluminum tanks, and most important, education of the pit crew and drivers to the dangers involved with methanol, are all used to reduce the potential hazards of a methanol fire rather than improving the flame luminosity of the methanol fuel. These safety measures are used to prevent fires rather than to affect the results of one. These safety measures will be discussed further in a subsequent section.

Several researchers have conducted a variety of experiments concerning the enhancement of the flame luminosity for methanol. Table 1 presents a list of potential flame luminosity enhancers examined in the studies, as well as other known luminosity enhancers found in this study.

There is no accepted standard for a visible flame. Coward and Woodhead[11] and Anderson and Siegl have determined the luminosity of a variety of hydrocarbons.[5] The results of these studies were normalized by Anderson and Siegl to isooctane and are presented in Table 2. From the table,

TABLE 2. RELATIVE RADIATION CHARACTERISTICS OF A VARIETY OF PURE HYDROCARBONS

	Normalized Relative Luminosity	
	Coward & Woodhead[11]	Anderson & Siegl[5]
i-octane	1.0	1.0 (defined)
Heptane	0.71	0.95
i-Pentane	--	0.6
Cyclohexane	0.83	0.71
Toluene	0.07[a]	0.70[a]
Benzene	0.07[a]	0.22[a]
Acetone	0.13	0.25
Methylethylketone	0.16	0.18
Ethyl Acetate	0.08	0.04
1-octanol	--	0.06
1-butanol	0.21	0.17
2-Methylpropanol	0.34	0.3
2-propanol	--	0.19
1-propanol	0.09	0.06
Ethanol	0.01	0.03
Methanol	0.01	0.0003

[a]Causes for the variations in the data are not readily apparent in the references.

TABLE 1. POTENTIAL FLAME LUMINOSITY ENHANCERS

Compounds	References
isopropyl alcohol	4
t-butanol	11
isopentane	5, 11
hexane	11
cyclohexane	12
toluene	6, 7, 8, 11, 12
xylene	11, 12
cat pentane[a]	11
light cracked naphtha[b]	11
hydroformate[c]	11
reformate[d]	13
unleaded gasoline	11, 13, 14
benzyl alcohol	9
xylenol (isomers)	16
anisole	16
ethoxybenzene	16
2-phenylethanol	16
o-ethylphenol	16
sodium acetate	12
metal-organic salts	12, 14
organometallic compounds	14
alkyl borates	10, 14

[a]Catalytic cracker fraction distilling in the range of 25-150°C
[b]Catalytic cracker fraction distilling in the range of 30-160°C
[c]Reformate fraction distilling in the range of 55-220°C
[d]Aromatic gasoline blending stock

isooctane (gasoline), ethanol and methanol have a 3000:1000:1 luminosity ratio while burning (i.e., a flame from burning gasoline is approximately three times more visible than an ethanol flame and 3000 times more visible than a methanol flame). Anderson and Nichols[8] adopted the luminosity of burning ethanol as a reasonable target for a visible flame. Most hydrocarbons function as methanol flame luminosity enhancers; however, concentrations of greater than 10 volume percent may be required to produce the desired effect. Anderson and Nichols indicate that 10 volume percent gasoline in methanol has a flame luminosity equal to that of pure ethanol.

In addition to enhancing the flame luminosity, a desirable characteristic of an additive would be the persistence of the visible flame until all of the liquid was consumed or the fire was extinguished. Any additive that does not provide a luminous flame for the entire length of the burn introduces the risk that the observer could be misled into believing that the flame is gone when the color disappears. Several investigators have examined the time-dependent, flame luminosity for a number of hydrocarbons mixed with methanol. The data from several such studies are tabulated in Table 3.

Anderson and Siegl[5] proposed that the time-dependent behavior is readily understood on the basis of the methanol/additive distillation curves, the concentration of the additive, and the volatility of the additive. Methanol forms minimum boiling azeotropes with many of the lower-molecular weight hydrocarbons. Upon burning a pool of liquid, the additive is selectively distilled from the liquid phase, which concentrates the methanol. After a sufficient quantity of the additive has been removed during the burning, the methanol dominates the liquid and the visible flame disappears. Agitation with a magnetic stirrer has no noticeable effect on either the total duration of the flame or the duration of the luminous flame. A comparison of additives with high and low volatility demonstrates the effect on the flame luminosity. A highly volatile, low boiling additive, such as isopentane, produces a short-duration, intensely-luminous flame. Once the isopentane burns away, the remainder of the flame is indistinguishable from a flame of burning neat methanol. An additive with a higher boiling point such as o-xylene, which does not form methanol azeotropes, was shown to have a low luminosity initially and become more luminous following selective distillation of the methanol from the liquid phase.

A list of azeotropes formed by methanol is included in Table 4. The only two compounds that form azeotropes at a methanol concentration of greater than 75 volume percent are methylal and nitromethane. Methylal does not burn with a visible flame, and would not itself enhance the flame luminosity of methanol. Methylal will be discussed further in a subsequent section. Nitromethane is used to increase power in drag racing applications, but it is not practical for use in street vehicles.

Keller, Nakaguchi, and Ware[6] indicated that the flame luminosity of methanol containing less than 5 volume percent light hydrocarbons was generally poor, while increasing the concentration of light hydrocarbons to 10 volume percent substantially increased the flame luminosity and visibility. Several methanol/pentane blends were examined for burning characteristics. The blends contained either 5 or 10 volume percent pentane as well as other

TABLE 3. TIME DEPENDENT FLAME LUMINOSITY WITH METHANOL

Additive	Volume % of Additive	% Flame Luminosity Time[a]	Comments
methanol	--	0	Not visible except in dark[4]
isopropyl alcohol	6	--	Light yellow flame barely visible[4]
t-butanol	6	--	Light yellow flame barely visible[4]
light hydrocarbons	5		Generally poor[6]
light hydrocarbons	10		Substantially improved[6]
DME[b]	5	0	(4)
isopentane	6	0	Few flashes of yellow[4]
isopentane + DME	2 5	0	Few flashes[4]
isopentane + toluene + DME	2 2 4.6	43	(4)
Hexane + DME	2 4	10	(4)
Cyclohexane	10	33	Flame luminosity decreased until it resembled burning methanol[5]
toluene	2	0	Few flashes of yellow[4]
toluene		90	Strong luminosity[5]
toluene + pentane	2 5		Substantially increased flame luminosity and visibility[6]
toluene + pentane	2 10		Substantially increased flame luminosity and visibility[6]
toluene + pentane	5 5	50	(6)
toluene + pentane	5 10	70	(6)

TABLE 3 (Cont'd). TIME DEPENDENT FLAME LUMINOSITY WITH METHANOL

Additive	Volume % of Additive	% Flame Luminosity Time[a]	Comments
toluene + DME	2 3.6	57	(4)
toluene + DME	2 5.4	83	Non-luminous in mid-period[(4)]
toluene + DME	4 3.9	82	(4)
toluene + DME	4 5.6	90	(4)
toluene + DME	6 6	89	(4)
toluene + LCN[c]	2 8	56	(4)
toluene + DME + LCN	2 4.5 2	73	(4)
toluene + DME + LCN	2 3.8 4	100	(4)
toluene + DME + LCN	2 4.9 4	100	(4)
toluene + DME + LCN	2 6 4	100	(4)
toluene + DME + xylene	1 6 1		(4)
toluene + DME + xylene	2 6 2	94	(4)
xylene	2	0	Few flashes of yellow[(4)]

TABLE 3 (Cont'd). TIME DEPENDENT FLAME LUMINOSITY WITH METHANOL

Additive	Volume % of Additive	% Flame Luminosity Time[a]	Comments
LCN + DME	2 5	0	Few flashes(4)
LCN + DME	4 4	23	(4)
LCN + DME	6 5.7	43	(4)
LCN + DME + hydroformate[d]	2 4 2	42	(4)
hydroformate	4	100	Light yellow flame(4)
hydroformate + DME	2 4.9	0	Few flashes(4)
hydroformate + DME	4 3.8	100	(4)
hydroformate + DME	4 4.9	100	(4)
hydroformate + DME	4 5.7	100	(4)
cat pentane[e] + DME	2 5	0	Few flashes(4)
cat pentane + DME	4 4	0	Few flashes(4)
unleaded gasoline (14.5 RVP)	6	50	Light yellow flame(4)
unleaded gasoline (14.5 RVP)	10	100	(4)
gasoline	10		Equal to burning neat ethanol(8)
gasoline	10	50	(6)
gasoline	15	100	(6)

TABLE 3 (Cont'd). TIME DEPENDENT FLAME LUMINOSITY WITH METHANOL

Additive	Volume % of Additive	% Flame Luminosity Time[a]	Comments
gasoline + pentane	5 5	20	Visible flame(6)
gasoline + pentane	5 10	30	Visible flame(6)
reformate[f] + pentane	5 5	20	Visible flame(6)
reformate + pentane	5 10	30	Visible flame(6)

[a]Portion of time that flame was yellow and clearly visible
[b]Dimethyl ether
[c]Light Cat Naphtha-Catalytic cracker fraction distilling in the range of 30-165°C
[d]Reformate fraction distilling in range of 55-220°C
[e]Catalytic cracker fraction distilling in the range of 25-150°C
[f]Aromatic gasoline blending stock

TABLE 4. AZEOTROPE SYSTEMS WITH METHANOL[12]

Compound	Boiling Point, C	Percent Composition			Specific Gravity
		Methanol	A	B	
Binary Systems					
Acetone	55.7	12.0	88.0		0.795
Acetonitrile	63.5	19.0	81.0		--
Benzene	58.3	39.5	60.5		0.844
Chloroform	53.5	13.0	87.0		1.342
1,1,-dichloroethane	49.1	11.5	88.5		--
Dimethyl acetal	57.5	24.2	75.8		0.841
Dimethyl formal	41.8	7.9	92.1		0.860
2,5-dimethyl furan	61.5	51.0	49.0		0.841
Ethyl acetate	62.1	48.6	51.4		0.846
Ethyl butyl ether	62.6	56.0	44.0		0.770
Ethylene dichloride	59.5	35.0	65.0		1.045
Ethyl formate	51.0	16.0	84.0		--
Heptane	59.1	51.5	48.5		--
Iodomethane	37.8	4.5	95.5		--
Isopropyl acetate	64.0	70.2	29.8		0.816
Methyl acetate	54.0	18.7	81.3		0.908
Methylal	41.8	92.2	7.8		--
Methyl acrylate	62.5	54.0	46.0		--
Nitromethane	64.5	92.0	8.0		--
Octane	63.0	72.0	28.0		--
Pentane[13]	31	7	93		
Toluene	63.7	72.4	27.6		0.813
Trichloroethylene	60.2	36.0	64.0		1.126
1,1,2-trichlorotrifluoroethane	39.9	6.0	94.0		1.476
Trimethyl borate	54.0	27.0	73.0		0.892
Vinyl acetate	58.5	36.6	63.4		0.880
1-methoxy-1,3-butadiene	62.0	57.5	42.5		--
Vinylbutryl ether	62.0	52.0	48.0		--
Ternary Systems					
Acetone	57.5	23.0	30.0		
Chloroform				47.0	
Acetone	51.5	16.0	43.5		
Cyclohexane				40.5	
Acetone	53.7	17.4	5.8		
Methyl acetate				76.8	0.898
Carbon disulfide	35.6	7.0	55.0		
Methylal				38.0	
Cyclohexane	50.8	17.8	33.6		
Methyl acetate				48.6	
Hexane	45.0	14.0	59.0		
Methyl acetate				27.0	0.73
Methyl chloroacetate	67.9	81.2	13.54		
Water				5.26	

additives for increasing the flame luminosity. The additives included toluene, gasoline, and reformate (an aromatic gasoline blending stock). Of these three, toluene was found to be the most effective in increasing flame luminosity. As little as 2 volume percent toluene substantially increased the persistence of the flame luminosity and the visibility for both methanol/pentane blends. When 5 volume percent toluene was added to both blends, the flame was visible until about 50 to 70% of the liquid was consumed. The addition of 5 volume percent gasoline or reformate was less effective, and the visible flame persisted only until 20 to 30% of the liquid was consumed. With 10 volume percent gasoline in neat methanol (without the additional pentane), the visible flame persisted until about 50% of the liquid was consumed. For the flame to last the entire length of the burn, 15 volume percent or more gasoline was required.

Panzer,[4] whose effort was mostly concerned with the use of dimethyl ether (DME) as a primer for good cold starting characteristics and water contamination tolerance, conducted a variety of experiments on the flame luminosity of methanol. The luminosity was evaluated by igniting 2 cc of each blend in a shallow aluminum dish. The dish was located in an unlit hood with a black background. The flame duration was perceived visually and recorded. Unleaded gasoline as well as some of its component distillation fractions were examined. Hydroformate, a reformate fraction distilling in the range of 55-220°C, produced a luminous flame throughout the entire burn at the lowest concentration (4 volume percent). A concentration of 10 volume percent unleaded gasoline was required to give a visible flame for the entire burn. Individual components, such as isopentane, toluene, xylene, and lower concentrations of unleaded gasoline, were not as effective in enhancing the flame luminosity.

Panzer[4] conducted a number of luminosity experiments on the effect of additives for DME/methanol blends. DME does not burn with a visible flame nor does it increase the flame luminosity of methanol alone. DME does appear to be involved with the length of time the flame is enhanced. This fact is illustrated in Table 3. A blend of 2 volume percent toluene with 8 volume percent LCN in methanol produced a visible flame during 56% of the burn time. When DME was present in a concentration of 6 volume percent, a visible flame was produced for 100% of the burn time with as little as 4 volume percent LCN and 2 volume percent toluene. Another example involved a blend of 2 volume percent toluene with DME in methanol. By increasing the DME concentration from 3.6 volume percent to 5.4 volume percent, the luminosity time increased from 57% to 83%. In this case, the flame was not visible during the middle of the burn time. A similar increase was observed for toluene with DME in methanol. The most effective additives in producing visible flames with the DME/methanol blends were hydroformate and a combination of toluene and light cat naphtha (LCN), a catalytic cracker fraction distilling in the range of 30-165°C. These DME/methanol/additive blends produced a visible flame for the entire burn. For example, a combination of 6 volume percent DME, 2 volume percent toluene, and 2 volume percent xylene gave a luminous flame for 94% of the burn time.

Panzer[4] also examined the effect of water on the luminosity of DME primed methanol. Table 5 presents a comparison of the luminosity data with and without water present. The addition of water to the blends containing

additives for increasing the flame luminosity. The additives included toluene, gasoline, and reformate (an aromatic gasoline blending stock). Of these three, toluene was found to be the most effective in increasing flame luminosity. As little as 2 volume percent toluene substantially increased the persistence of the flame luminosity and the visibility for both methanol/pentane blends. When 5 volume percent toluene was added to both blends, the flame was visible until about 50 to 70% of the liquid was consumed. The addition of 5 volume percent gasoline or reformate was less effective, and the visible flame persisted only until 20 to 30% of the liquid was consumed. With 10 volume percent gasoline in neat methanol (without the additional pentane), the visible flame persisted until about 50% of the liquid was consumed. For the flame to last the entire length of the burn, 15 volume percent or more gasoline was required.

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luminosity additives with DME as a cosolvent had no effect on the water tolerance (phase stability); however, the luminosity was found to decrease as the water concentration was increased. Panzer suggested that the hydroformate/methanol blend should not contain more than 5 volume percent water, and that LCN/methanol blends should not contain more than 3 volume percent water. An increase in the water concentration from 5 to 10 volume percent with a small increase in the DME concentration (5.0 to 6.3 volume percent) decreased the percent of luminosity time from 100% to 65%. A similar effect was observed for DME/toluene/LCN blends.

TABLE 5. EFFECT OF WATER ON LUMINOSITY OF DIMETHYLETHER-PRIMED METHANOL

Composition, Volume Percent					Luminosity
DME	Toluene	Hydroformate[a]	LCN[b]	Water	Time, %[c]
	2				0
3.9	4				82
5.6	4				90
5.6	4			10	62
		4			100
3.8		4			100
4.9		4			100
5.7		4			100
5.0		4		5	100
6.0		4		7	85
6.3		4		10	65
		2	8		56
3.8		2	4		100
4.9		2	4		100
6		2	4		100
4.9		2	4	3	100
3.9		2	4	5	73
5.5		2	4	7	69
6.0		2	4	10	55

[a]Reformate fraction distilling in the range 55-220 C
[b]Catalytic cracker fraction distilling in the range 30-165 C
[c]Portion of time that flame is yellow and clearly visible

In addition to DME as a cosolvent for luminous flame additives, several authors have suggested that other alcohols could be used as cosolvents with methanol. Panzer[4] examined the flame luminosity of two low molecular weight alcohols: isopropyl and t-butyl alcohol. Neither of these two neat alcohols was effective in providing an adequate luminosity at the concentration selected (6 volume percent). Although simple alcohols do not contribute significantly to the flame luminosity, these compounds may serve as cosolvents

for other luminous flame additives. Panzer did not pursue the use of alcohols for cosolvents.

Higher molecular weight alcohols as cosolvents would help to reduce the sensitivity of methanol/nonpolar hydrocarbon blends to water and increase the solubility of these hydrocarbons in the methanol. The most effective cosolvent for methanol/gasoline blends are C_3 to C_8 aliphatic alcohols. The effectiveness of cosolvent alcohols increases with chain length to at least C_6, and decreases with branching. The effectiveness is also greater for primary than for secondary or tertiary alcohols. Keller, Nakaguchi, and Ware[6] conducted a number of cosolvent experiments on the effect of water tolerance for 10 volume percent methanol blended with gasoline. The alcohols included a C_2 - C_4 alcohol mixture, isobutanol (C_4), amyl alcohol (C_5), and 2-ethylhexyl alcohol (C_8). The transition temperature range, the temperature range at which the initial appearance of turbidity or visible phase separation occurred, was determined for each alcohol blend with either 0.25 or 0.50 weight percent water present. Although these experiments were conducted on gasoline rich blends, one would expect similar results for methanol fuels. No flame luminosity studies were conducted by Keller, Nakaguchi, and Ware, but azeotrope formation with alcohols and flame additives could help to enhance the visible flame characteristics. No experimental investigations have been conducted about the effect of increased flame luminosity of alcohols, other than rudimentary studies by Coward and Woodhead[11], Anderson and Siegl[5], and Panzer.[4]

Another means of increasing the flame visibility of methanol involved the addition of organometallic compounds and/or metal organic salts. In a flame, metal atoms are excited and emit radiation at visible wavelengths. Anderson and Siegl[5] examined sodium acetate, a metal-organic salt, as a flame luminosity enhancer for methanol. Sodium acetate is an ingredient in Sterno, a commercially available methanol fuel for heating. The problem encountered by Anderson and Siegl with sodium acetate, as an additive to methanol, was the inverse relation between concentration of the compound in solution (i.e., intensity of the visible radiation in the flame) and the volatility of the compound. As the flame burned, the metal organic salt was concentrated in the liquid phase by selective distillation of the methanol, and it precipitated out when the solubility product was exceeded. Other organometallic compounds such as tetraethyllead have been used in leaded gasolines for a number of years, but are slowly being phased out. It is unlikely, however, that organometallic compounds would produce the desired effect at concentrations that would be reasonable in motor fuel. In addition, many metals are detrimental to the operation of engines and exhaust systems of modern catalyst-equipped vehicles.

Alkyl borates and boron esters have been proposed as a means of enhancing the flame luminosity of methanol.[14] Borates burn with a yellowish green flame when combined with alcohol.[12] Blends of alkyl borates have also been suggested as water scavengers in 85% gasoline/15% methanol blends in a German patent.[10] The blends in the patent contained between 0.5 and 1.5 weight percent trialkyl borate compounds. Alkyl borates in this concentration range are not expected to enhance the visible flame characteristic of methanol.

There are other potential flame enhancers based on some of the same chemical and physical properties suggested in the literature. These compounds include benzyl alcohol, anisole, o-ethylphenol, ethoxybenzene, 2-phenylethanol, and the isomers of xylenol. No specific reference was found for which these compounds were tested in methanol flames. They would take advantage of high aromaticity, and yet be miscible with methanol. Additional candidates would include compounds such as naphthalenes, phenols, and other substituted aromatics.

B. Evaluation

As indicated in the literature, there are a number of compounds that can be added to methanol to increase its flame luminosity. Hydrocarbons, especially those with a high aromatic content, appear to give the best results when added to methanol. The aromatics form soot particles in flames, which emit visible "grey-body" radiation. Aliphatic hydrocarbons also produce visible flames, but their effects on the flame luminosity are not as significant until the aliphatic hydrocarbon reaches a chain length of six or more carbons.

In addition to producing a highly visible flame, another key consideration in selecting an additive is the length of time the flame is visible while methanol is burning. If the luminosity ceases before the source of the fire is determined, a fire-fighter may be misled into thinking that the flame has been extinguished. Highly complex mixtures of hydrocarbons appear to be the most likely additives for enhancing flame luminosity for the duration of a methanol fire. These mixtures form a number of azeotropes with methanol, which burn with a visible flame that persists throughout the time of the fire.

Panzer[4] found that a reformate fraction distilling in the range of 55-220°C was the best flame enhancer at the lowest concentrations. As little as 4 volume percent hydroformate produced a light-yellow, visible flame for 100 percent of the burn time. Unleaded gasoline at a concentration of 10 volume percent was also found to produce a visible flame for 100 percent of the burn. Keller, Nakaguchi, and Ware[6], however, found that as much as 15 volume percent of gasoline was required to produce a luminous flame during 100 percent of the burn time. The difference between the findings of these two researchers may be due to the qualitative definition of a luminous flame.

When considering an additive to enhance flame luminosity, 10 to 15 volume percent of unleaded gasoline appears to be a likely candidate. Large quantities of unleaded gasoline could be readily made available for mixing with methanol, and the necessity of building additional facilities to produce a special methanol additive would be avoided. There would be some increase in the cost of a methanol fuel with the addition of unleaded gasoline, depending on the amount of unleaded gasoline added (10 to 15 percent). Using the average 1983 Gulf Coast spot barge price for methanol, 44¢ per gallon (ranged from 41 to 47¢ per gallon[15]), and an average 1983 Gulf Coast refinery price for unleaded gasoline, 84¢ per gallon (ranged from 72 to 88¢ per gallon[16]), the addition of 10 volume percent unleaded gasoline to methanol would increase the bulk rate cost of the methanol by about 4¢ per gallon, or about 9 percent (addition of 15 volume percent unleaded gasoline would increase the cost by 6¢ per gallon, or 14 percent). This estimate assumes that the mixing would be carried out using

pipelines, and that the cost of mixing would be small when compared to the cost of the fuels. The higher energy content of the added gasoline (approximately 113,000 BTU/gal as compared to 56,100 BTU for methanol) would largely offset the cost increase of adding the gasoline.

If cosolvents are used to increase the water tolerance of the methanol/unleaded gasoline blend, additional costs would be incurred. Keller, Nakaguchi, and Ware[6] estimated that a mixture of C_2-C_4 alcohols produced in fuel grade methanol (without purification) by using a non-selective catalyst would cost about 1.62 times as much as methanol or about 72¢ per gallon (1978 estimate). Therefore, each 10 percent of cosolvent added would raise the cost of methanol by about 3¢ per gallon.

The addition of complex mixtures of hydrocarbons, such as unleaded gasoline, to increase the flame luminosity of methanol also aids in other safety-related areas. One of these areas is the flammability of the methanol vapor in a closed system. Methanol in the vapor state is flammable over a wide range of temperatures and concentrations. The flammability limit for methanol in air ranges from about 36 volume percent as an upper limit to about 6 volume percent as a lower limit. Below the lower flammability limit, the vapor is to lean to burn; above the upper limit, it is too rich. By comparison, gasoline has as much narrower flammability range, with an upper limit of 7.6 percent and a lower limit of 1.4 percent.

Keller, Nakaguchi, and Ware[6] found that when 5 to 10 volume percent of C_5 to C_7 hydrocarbons was added to methanol, the resultant vapor exceeded the upper flammability limit (i.e., became too rich to ignite when the temperature of the methanol/hydrocarbon mixture was maintained at or above -20°C). They found that when 20 volume percent gasoline was used as a blending agent, the vapor concentration exceeded the upper flammability limit above -10°C; and that with 25 percent gasoline, the vapor concentration exceeded the upper flammability limit when the fuel mixture was above -30°C. Other researchers have produced similar results. Thus, the addition of 10 percent or more unleaded gasoline or other hydrocarbon mixtures would reduce the possibility of an explosion in the vapor space of a closed space such as vehicle fuel tank.

Another problem associated with methanol fuel that would be aided by the addition of a complex hydrocarbon mixture is the vehicle cold startability, i.e., the ability to start an engine at low ambient temperatures (Keller, Nakaguchi, and Ware[6] have defined low ambient temperatures as anything below 10 to 16°C). The problem is related to methanol's relatively high latent heat of vaporization (506 BTU/lb as compared to 150 BTU/lb for gasoline). Keller, Nakaguchi, and Ware[6] indicated that the addition of 5 volume percent pentanes or 12 volume percent gasoline to methanol gave adequate vehicle cold startability at temperatures down to -10°C. For temperatures down to -30°C, 8-10 volume percent pentanes or 25-30 volume percent gasoline was necessary for adequate vehicle cold startability. A combination of 15 volume percent gasoline and 4 volume percent pentanes provided adequate cold startability down to -29°C.

The addition of gasoline or a hydrocarbon mixture to methanol would result in some change in the exhaust emissions from the engine. Carburetor or injection system adjustment, along with the use of emission control systems found on current vehicles, could minimize differences between the regulated emissions (hydrocarbons, carbon monoxide, and oxides of nitrogen) from vehicles using pure methanol fuel and those from vehicles fueled with methanol/hydrocarbon blends. Other exhaust emissions such as those related to sulfur content (sulfate, sulfur dioxide, etc.) and aromatics (particulates, benzene, etc.) would increase as a function of their concentrations in the additive (i.e., hydrocarbon) material. Aldehyde emissions may be reduced by the addition of hydrocarbon mixtures to methanol, but an effective vehicle catalytic converter could render these differences negligible. On the negative side, the addition of hydrocarbon mixtures to methanol fuel would result in an increase in the evaporative emissions throughout the fuel supply system and possibly even for refueling emissions.[6,17] Concern over this problem is increased by the fact that many of these hydrocarbons are known to be more reactive in photochemical smog formation than neat methanol. A number of researchers have conducted air-quality modeling calculations and shown that substitution of methanol fuel for gfasoline in the calculations would lead to a reduction in the ozone concentration. These researchers conclude that methanol would have a very beneficial impact on the air quality and deserves further investigation.[18,19,20]

The toxicity of methanol, along with its lack of taste and low odor intensity are health effects problems that could be associated with the use of methanol as a motor fuel. In general, the addition of a complex mixture of hydrocarbons, such as gasoline, is expected to result in an increase in odor and taste intensity. The addition of gasoline (15 volume percent) to methanol had been reported to give the mixture a slight but noticeable odor; and when the methanol/gasoline blend is mixed with water, to give an unattractive milky mixture with a strong odor of gasoline.[6]

III. TASTE DETERRENTS

Of the three major routes of methanol poisoning (ingestion, inhalation and subcutaneous absorption), direct ingestion is the quickest. Methanol does not have a strong or distinctive taste to identify its presence. In fact, it has been mistaken for ethanol innumerable times, and consumed with sometimes disastrous consequences. The addition of a bitter or foul tasting substance would help to deter accidental poisoning and possibly even prevent some intentional ingestion of methanol fuel.

A. Literature Search

Hagen[21], and Wimer, Russell and Kaplan[22] have stated that the usual fatal dose by direct ingestion of methanol is between 50 to 100 ml (2-4 oz.), although 25-50 ml (1-2 oz.) has often been fatal if not treated immediately. The lowest reported fatal dose was 3 teaspoons (about 15 ml) of 40% methanol (approximately 6 ml of pure methanol) and the highest dose of a survivor was one pint (500 ml) of the same material (approximately 200 ml of pure methanol). Midwest Research Institute has stated that the chance of a 6 ml dose causing death is exceedingly low.[23] The consumption of ethanol prior to or in conjunction with methanol has been found to decrease the toxic effect. Ethanol has been shown to compete effectively for the enzyme responsible for the conversion of methanol to formaldehyde and formic acid. The production of formaldehyde and formic acid is suspected of being responsible for some of the toxic effects of methanol.

Although little information exists on the addition of materials to methanol to make it undrinkable, denaturants have been added to commercial ethanol to render it unfit for human consumption for over 60 years. A list of denaturants that have been used in ethanol is presented in Table 6. Although denaturants are most commonly involved with ethanol, many of these substances could be used in methanol as a taste deterrent.

The two categories of denaturing formulas for ethanol are (1) completely denatured alcohol (C.D.A.), and (2) specially denatured alcohol (S.D.A.). Completely denatured alcohol is ethanol which has denaturants added to render it entirely unfit for human consumption. This type of denatured alcohol may be handled for legitimate purposes without filing a bond, obtaining a permit or paying a tax. Specially denatured alcohol has been denatured so that it can be used for a special purpose and may be received and blended at bonded facilities that are subject to rigorous inventory control and government supervision. Two C.D.A. and three S.D.A. formulas have been authorized by the Federal government for ethanol use as a fuel. These are listed in Table 7. The Southwest Alabama Farmer's Cooperative Association also evaluated a denatured ethanol formula for use in farm equipment.[25] In addition, several foreign patents exist for denaturing fuel and ethanol. Methanol is included as a denaturant for ethanol in several of these formulas. Ethanol, on the other hand, cannot be used as a denaturant for methanol. Ethanol has, however, been used in the treatment of methanol poisoning victims, and has been reported to help reduce the effects of methanol poisoning. Only one of the formulas in Table 7 contains substances other than gasoline and/or methanol. Many other S.D.A.

TABLE 6. U.S. GOVERNMENT-AUTHORIZED DENATURANTS FOR COMPLETELY DENATURED ALCOHOL (C.D.A.) AND SPECIALLY DENATURED ALCOHOL (S.D.A.)[24]

DENATURANT	USED IN
Acetaldehyde	S. D. 29
Acetone N. F.	S. D. 23-A; 23-H
Acetaldol	C. D. 18
Almond oil, bitter N. F.	S. D. 38-B
Ammonia solution, strong U. S. P.	S. D. 36
Anethole U. S. P.	S. D. 38-B
Anise oil U. S. P.	S. D. 38-B
Bay oil (myrcia oil) N. F.	S. D. 23-F; 38-B; 39-D
Benzaldehyde N. F.	S. D. 38-B
Benzene	S. D. 2-B; 2-C; 12-A
Bergamot oil N. F.	S. D. 23-F; 38-B
Bone oil (Dippel's oil)	S. D. 17
Boric acid U. S. P.	S. D. 38-F
Brucine alkaloid	S. D. 40
Brucine sulfate N. F. IX	S. D. 40
n-Butyl alcohol	S. D. 44
tert-Butyl alcohol	S. D. 39; 39-A; 39-B; 40; 40-A
Camphor U. S. P.	S. D. 27; 27-A; 38-B
Caustic soda, liquid	S. D. 36
Chloroform	S. D. 20
Chlorothymol N. F.	S. D. 38-B; 38-F
Cinnamon oil (cassia oil) U. S. P.	S. D. 38-B
Citronella oil, natural	S. D. 38-B
Cinchonidine	S. D. 39-A
Cinchonidine sulfate N. F. IX	S. D. 39-A
Cinnamic aldehyde (cinnamaldehyde) N. F. IX	S. D. 38-B
Clove oil U. S. P.	S. D. 27-A; 38-B
Coal tar U. S. P.	S. D. 38-B
Diethyl phthalate	S. D. 39-B; 39-C
Ethyl acetate	S. D. 35; 35-A
Ethyl ether	S. D. 13-A; 19; 32
Eucalyptol U. S. P.	S. D. 37; 38-B
Eucalyptus oil N. F.	S. D. 38-B
Eugenol U. S. P.	S. D. 38-B
Formaldehyde solution U. S. P.	S. D. 22; 38-C; 38-D
Gasoline	S. D. 28-A
Glycerol U. S. P.	S. D. 31-A
Guaiacol N. F.	S. D. 38-B
Iodine U. S. P.	S. D. 25; 25-A
Kerosene	C. D. 18; 19
Lavender oil U. S. P.	S. D. 27-B; 38-B
Menthol, U. S. P.	S. D. 37; 38-B; 38-C; 38-D; 38-F
Mercuric iodide, red N. F.	S. D. 42
Methylene blue N. F.	S. D. 4
Methyl alcohol	S. D. 3-A; 30
Methyl isobutyl ketone	C. D. 18; 19; S. D. 23-H
Methyl violet (methylrosaniline chloride)	S. D. 33
Methyl violet (methylrosaniline chloride) U. S. P.	S. D. 33
Mustard oil, volatile (allyl isothiocyanate), U. S. P. XII	S. D. 38-B
Nicotine solution	S. D. 4
Peppermint oil U. S. P.	S. D. 38-B
Phenol U. S. P.	S. D. 38-B; 46
Phenyl mercuric benzoate	S. D. 42
Phenyl mercuric chloride N. F. IX	S. D. 42
Phenyl mercuric nitrate N. F.	S. D. 42
Phenyl salicylate (salol) N. F.	S. D. 38-B
Pine needle oil, dwarf N. F.	S. D. 38-B
Pine oil, N. F.	S. D. 38-B
Pine tar, N. F.	S. D. 3-B
Potassium iodide, U. S. P.	S. D. 25; 25-A; 42
Pyridine bases	S. D. 6-B
Pyronate	C. D. 18
Quassia, fluid extract of, N. F. VII	S. D. 39
Quassin	S. D. 40
Quinine, N. F.	S. D. 39-A
Quinine bisulfate N. F.	S. D. 39-A; 39-D
Quinine hydrochloride U. S. P.	S. D. 39-A
Quinine sulfate U. S. P.	S. D. 39-D
Resorcin, U. S. P.	S. D. 23-F
Rosemary oil, N. F.	S. D. 27; 38-B
Rubber hydrocarbon solvent	S. D. 2-B; 2-C
Safrol	S. D. 38-B
Salicylic acid, U. S. P.	S. D. 23-F; 39
Sassafras oil, N. F.	S. D. 38-B
Shellac (refined)	S. D. 45
Sodium iodide, U. S. P.	S. D. 25; 25-A
Sodium, metallic	S. D. 2-C
Sodium salicylate, U. S. P.	S. D. 39; 39-D
Soap, hard, N. F.	S. D. 31-A
Soap, medicinal soft, U. S. P.	S. D. 27-B
Spearmint oil, N. F.	S. D. 38-B
Spearmint oil, terpeneless	S. D. 38-B
Spike lavender oil, natural	S. D. 38-B
Storax, U. S. P.	S. D. 38-B
Sucrose octa-acetate	S. D. 40-A
Thimerosal, N. F.	S. D. 42
Thyme oil, N. F.	S. D. 38-B
Thymol, N. F.	S. D. 37; 38-B; 38-F
Tolu balsam, U. S. P.	S. D. 38-B
Turpentine oil, N. F.	S. D. 38-B
Vinegar	S. D. 18
Wintergreen oil (Methyl salicylate) U. S. P.	S. D. 38-B, 46
Wood alcohol	S. D. 1

TABLE 7. DENATURANT FORMULAS FOR ETHANOL AND OTHER FUELS

1. C.D.A. Formula No. 18: to every 100 gallons of ethyl alcohol of not less than 160 proof, add:

   - 2.50 gallons of methyl isobutyl ketone;
   - 0.125 gallon of pyronate or a compound similar thereto;
   - 0.50 gallon of acetaldol (b-hydroxybutyraldehyde); and
   - 1.00 gallon of either kerosene, deodorized kerosene, or gasoline.

2. C.D.A. Formula No. 19: to every 100 gallons of ethyl alcohol of not less than 160 proof, add:

   - 4.0 gallons of methyl isobutyl ketone; and
   - 1.0 gallon of either kerosene, deodorized kerosene, or gasoline.

3. S.D.A. Formula No. 1: to every 100 gallons of ethyl alcohol of not less than 185 proof, add:

   - 5.0 gallons wood alcohol.

4. S.D.A. Formula No. 3-A: to every 100 gallons of ethyl alcohol of not less than 185 proof, add:

   - 5.0 gallons methyl alcohol.

5. S.D.A. Formula No. 28-A: to every 100 gallons of ethyl alcohol of not less than 185 proof, add:

   - 1.0 gallon of gasoline.

6. Southwest Alabama Farmers' Cooperative Association[25] Formula is 10 gallons of denaturant blended with 90 gallons of gasoline.

   - 89.5 gallons of S.D.A. Formula No. 28-A,
   - 5.0 gallons gasoline,
   - 0.5 gallon methyl isobutyl ketone or tertiary butyl alcohol,
   - 5.0 gallons methyl alcohol,
   - a dye to color the solution.

TABLE 7 (Cont'd). DENATURANT FORMULAS FOR ETHANOL AND OTHER FUELS

7. French patent for denaturing fuel [26]

- 100 wt. parts dye (1-(2'-methyl-1'-phenyl-4-azophenylazo)-2-naphthalenol or 1,4-bis(butylamino)anthraquinone)
- 500 wt. parts diphenylamine
- 5-30 wt. parts 3-(oleylamino) propyl amine dioleate
- dilute to 1 g dye/hectoliter of fuel
- sometimes add 0.5-1 g furfural/hectoliter fuel

8. Polish patent[27]

The following by-products of the chemical industry are used as denaturants. The denaturant is a mixture of two or more components:

- aromatic fraction obtained by separation of gasoline and pyrolysis products
- ketone oil isolated from wood tar containing alcohols, aldehydes and ketones
- cumene fraction obtained by alkylation of C_6H_6
- fraction of higher aliphatic alcohols from oxo synthesis
- gasoline fraction with boiling point between 90-150 C containing 70% paraffins and 20% naphthenes

One part denaturant added to 99 parts ethanol colored with 18 mg/l of crystal violet.

formulas have been authorized by the Federal government, but they have specific uses ranging from the production of adhesives and binders to the production of vitamins.

In the 1920's, two ethanol base fuels were produced. One, called Alcogas, was manufactured by the U.S. Industrial Alcohol Company of New York and Baltimore. Alcogas contained 33% 180-190 proof ethanol, 35% gasoline, 25% benzene, and 7% ether. The other fuel, natalite, was made from molasses at Natal, South Africa. It consisted of 54-60% 190 proof ethanol, 45.8-39% ether, 0.15-1% pyridine, ammonia or trimethylamine, and 0.5% arsenious acid.[25] During the 1930's, ethanol was denatured in England by adding a small percentage of pyridine and wood naphtha.[28] However, this formula was not released from the surveillance of the Excise authorities until at least 25% hydrocarbons (benzene or gasoline) was mixed with the ethanol.

Mueller Associates, Inc.[25] listed several important technical factors involved in choosing a suitable denaturant for alcohol fuels. The alcohol fuel:

1. Should closely match the thermal and physical properties of the alcohol to ensure compatibility with the combustion characteristics.

2. Should add to the energy content; preferably in an amount greater than that required to produce the substance.

3. Should impart a taste or smell sufficiently disagreeable to discourage human consumption even if diluted, sweetened or flavored.

4. Should not be capable of being eliminated easily by filtration, distillation or any other process.

5. Should be capable of being easily and reliably detected.

6. Should not appreciably add to the emission levels from the products of combustion.

7. Should not leave any objectionable residue to clog or corrode fuel systems.

8. Should be readily available.

9. Should not add appreciably to the cost.

10. Should not complicate the regulatory compliance.

The Mueller Associates, Inc. paper was primarily concerned with ethanol; however, the technical factors should also be applicable to methanol.

Nakaguchi, Keller and Wiseman[29] conducted recovery experiments on various denatured ethanol blends (C.D.A. 19-A, S.D.A. 28-A, and the Southwest Alabama Farmer's Cooperative Association formula with the t-butyl alcohol option). The blends were washed with water to remove the gasoline and

extracted with a volatile stove and lantern fuel. The extracted alcohol was air blown until no hydrocarbon odor was detected. The results showed that the ethanol recovered from the blends might be deemed sufficiently palatable to drink by a determined consumer even though small amounts of noxious compounds remained. Similar experiments were conducted with six additional compounds as denaturants. These compounds were dimethylformamide (DMF), isopropyl alcohol, n-butyl alcohol, iso-amyl alcohol, t-butyl mercaptan, and an odorant (Sindar deodorant oil GD-64262). Of these six compounds ,the most effective denaturant was found to be DMF. It imparted a highly objectionable and bitter taste to the extracted alcohol. Although these tests were conducted with ethanol, similar results may be expected with methanol.

Keller, Nakaguchi, and Ware[6] have stated that the toxicity of a blend of gasoline and methanol is only slightly more of a hazard than ordinary gasoline. This is due to the prominent gasoline odor in the blend and the difficulty in separating methanol from the blend by "casual" means to be pure enough to be consumable. The addition of water to a gasoline (5 or more volume percent) and methanol blend was found to produce an unattractive milky mixture. Lower concentrations of gasoline were found to be not as objectionable, although the gasoline odor was still noticeable.

Methylal, which has been added to fuel methanol to increase the engine cold starting properties, is another additive which could be considered as a taste deterrent. In April, 1983, the New Gasoline Corp. of Arlington, Massachusetts was preparing to market the fuel Hydrolene, which contains up to 10% dimethoxymethane (methylal) blended with methanol.[30] Celanese and Bank of America have also expressed interest in producing blends of methylal and methanol.[31] Although no claims were made by any of these companies about the effect on the taste of methylal/methanol blends, methylal should act as a deterrent to the ingestion of methanol because of its pungent taste and chloroform-like odor.

A number of other compounds have been proposed and used as additives to produce a foul- or bitter-tasting product. Several of these compounds are listed in Table 8, along with their bitterness thresholds (if available), which are indications of the minimum concentration required to produce a bitter taste. Proctor and Gamble uses the additive Bitrex (denatonium benzoate) in a number of its detergent and household cleaning products to prevent unintentional ingestion.[33] Bitrex has been found to be 20 times as bitter as strychnine,[34] and is considered the most bitter substance known to man.[32] In one study, the addition of 0.00114% Bitrex was found to significantly reduce the amount of liquid dishwashing detergent consumed by 18- to 47-month-old children.[35] Bitrex is used as a taste deterrent in a number of other applications, including paints,[36,37,38] herbicides,[39], insecticides,[40] nailbiting and thumbsucking deterrent drugs,[41] rubbing alcohol,[34] vegetable oils,[40] and ethanol used for alcoholic toilet preparations and related articles.[43,44,45] The use of Bitrex is effective in concentrations of 2 to 3 mg/liter and is desirable due to the minimal residue left after evaporation.

Brucine, quassine, and sucrose octaacetate are other commonly used taste deterrents which have been used in some or all of the following products: hair and scalp preparations, lotions and creams for the head, face and body,

TABLE 8. COMPOUNDS FOR FOUL TASTE[32]

Compound	Bitterness Threshold	Comments
Absinthin	1:70,000	very bitter; chief bitter principle of wormwood
Aldehol		disagreeable odor; for denaturing alcohol (ethanol)
Benzyl alcohol		sharp burning taste; faint aromatic odor
Benzyl benzoate		sharp burning taste; pleasant aromatic odor
Benzthiazide		bitter taste
Bitrex	1:1,000,000	most bitter substance known to man. Added to toxic substances as a deterrent to accidental injestion
Brucine	1:220,000	very bitter taste; very poisonous; used in denaturing alcohols and oils
Capsaicin	1:100,000	burning taste
Collinsonia extract		peculiar odor; bitter, astringent taste
Columbin	1:60,000	major bitter principle from the root of Jatrorrhiza palmata Miers; very bitter
Condurangin	1:20,000	bitter principle from Condurango bark; astringent, aromatic bitter
Dimethylformamide		universal organic solvent; faint amine odor
Ethyl citrate		bitter oily liquid
Furfuryl alcohol		bitter taste; faint burning odor; poisonous
Humulon		bitter taste especially in alcoholic solutions

TABLE 8 (Cont'd). COMPOUNDS FOR FOUL TASTE

Compound	Bitterness Threshold	Comments
Isovaleric acid		acid taste; disagreeable rancid-cheese odor
Lupulon		bitter taste especially in alcoholic solutions
Marrubiin		diterpen lactone principle isolated from white horehound
o-(p-methoxybenzonyl)		bitter taste if used in concentrations exceeding 0.2 g/l
Methylal		pungent taste; chloroform odor; volatile flammable liquid
Methylarbutin		bitter
Methylbenzethonium chloride		bitter taste
Oleoresin of aspidium		bitter, unpleasant taste
Pyrazole		bitter taste; pyridine-like odor
Pyridazine		
Pyridine		sharp taste; characteristic disagreeable odor; flammable, colorless liquid
Quassin	1:60,000	one of the bitter constituents of the wood of Quassia amara L; very bitter
Quinidine sulfate		very bitter
Quinine	1:30,000 (quinine hydrochloride)	most important alkaloid of cinchona bark; salts also bitter
Strychnine	1:130,000	very bitter; extremely poisonous
Surcrose octaacetate		intensely bitter; hygroscopic; denaturant for alcohol (ethanol)
Vaccinum		bitter taste

deodorants for the body, perfumes, shampoos, soap and bath preparations, external pharmaceuticals, disinfectants, insecticides, fungicides and other biocides, and cleaning solutions including household detergents.

B. Evaluation

The practice of adding taste deterrents to products for use by the general public has been used by manufacturing companies for a number of years to increase the safety of their product. Taste deterrents have been added to everything from laundry detergents to perfumes, to prevent unintentional ingestion. Denaturants (which include taste deterrents) have been used routinely to prevent the consumption of ethanol. In addition to imparting a foul or bitter taste, an additive for methanol in a motor fuel application must be compatible with the engine and fuel system components, difficult to separate from the methanol, and economical in cost.

The addition of gasoline to methanol as a taste deterrent has been suggested by a number of researchers, and it meets a number of the criteria established for additives to fuel alcohols. Gasoline has also been used as a denaturant for ethanol in a number of applications. The addition of gasoline (15 volume percent) to methanol has been reported to give the mixture a slight but noticeable odor; and when the methanol/gasoline blend is mixed with water, to give an unattractive mixture with a strong odor of gasoline.[6] The use of gasoline as an odorant for methanol will be discussed in more detail in a subsequent section. Keller, Nakaguchi, and Ware[6] indicated that gasoline/methanol blends are only slightly more toxic than gasoline alone, and the methanol is difficult to separate from the gasoline in a potable form. They also stated that one would have to be "determined" to drink methanol with even as little as 1 to 2 percent gasoline added as a denaturant. The impact of gasoline as an additive on the cost of methanol, on the vehicle exhaust emissions, and on other safety-related areas has been discussed in detail in a previous section.

There are a number of compounds that can be added to give methanol a highly bitter and foul taste. The cost for several of these additives are listed in Table 9. While these compounds are very effective in imparting a bitter taste to methanol, they may need to be used in conjunction with other additives because they may be selectively removed from methanol by distillation. Bitrex is the most economical of the additives listed in Table 9, due to its relatively low bitterness threshold and corresponding low cost in use. Bitrex is currently used in paints, detergents and many other household materials, and is expected to be available in sufficient quantities to be used in a fuel application. Several of the other taste deterrents (sucrose octaacetate, brucine, quassin, and quinine) do not appear to be as practical or economical as Bitrex. The production of brucine, quassin, and quinine is dependent on environmental factors (the uncertainty of the raw material yield at harvest), and current supplies often do not meet the demand. An additional demand as a fuel additive could produce a severe shortage for other areas of use. Some of the taste deterrent additives are highly toxic (e.g. brucine and strychnine), and their use is not recommended for this reason. One pound of sucrose octaacetate (homologous to sugar) is required to denature 100 gallons of ethanol in toiletries, shampoos, etc. If an equivalent amount is required to denature fuel

methanol, use of the resulting mix could cause excessive engine wear and carbon deposit buildup in the same way that other sugar compounds do.

TABLE 9. CURRENT COSTS OF SEVERAL WIDELY USED TASTE DETERRENTS

Compound	Bulk Price	Cost Increase/Gallon of Methanol
Bitrex	$14 - 17/oz.	2¢
Sucrose octaacetate	$0.38/oz.	6¢
Brucine	$3-5/oz.	6¢
Quinine hydrochloride	$2-3/oz.	$1.50
DMF	$3.85/gallon	17¢
Methylal	$2.60/gallon	21¢

The cost of Bitrex is expected to have only a small effect on the cost of methanol fuel produced in bulk quantities. Bitrex is effective as a partial denaturant in ethanol toilet preparations and vegetable oils at concentrations not less than 2 ppm.[42,43,44] At the current market price for Bitrex, $14/oz,[46] the cost of adding this concentration of Bitrex to methanol fuel would be on the order of 0.4¢/gallon. A denaturing formula authorized for fuel ethanol requires the use of 1/8 oz of Bitrex for every 100 gallons of ethanol (9 ppm).[47] If a similar formula is appropriate for use with methanol fuel, the cost of adding Bitrex would be on the order of 2¢ per gallon. This approximately five-fold increase in the concentration of Bitrex over the minimum recommended concentration (2 ppm) would help to deter the dilution of fuel methanol with water or other beverages to make the mixture more palatable. The costs associated with blending Bitrex and methanol are estimated to be on the order of 0.1¢ per gallon.[48] The impact of Bitrex on exhaust emissions is unknown, but due to the low concentrations of Bitrex necessary to provide a bitter taste in methanol (2-9 ppm), the exhaust emissions would not be expected to differ significantly from those of pure methanol.

Other compounds that have been suggested as possible taste deterrents for methanol include dimethylformamide (DMF) and methylal. DMF was examined by Nakaguchi, Keller, and Wiseman[29] for denaturing ethanol, and methylal has been proposed as a cold-starting additive for fuel methanol. Both compounds are foul-tasting, and would deter the consumption of methanol. The New Gasoline Corporation of Arlington, Massachusetts has estimated that a 10% methylal/90% methanol fuel could be produced for 45¢/gallon based on a Gulf coast spot-barge price of 43¢/gallon for methanol.[30] This estimate is based on a bulk methylal price of 60 to 65¢ per gallon. However, the current price of methylal, $2.60 per gallon, would increase the cost of methanol by 21¢ per gallon (48 percent increase). The addition of 5 volume percent of DMF at

$3.85/gallon to methanol would result in an increase of 17¢ per gallon based on current DMF costs.

Both DMF and methylal are low molecular weight compounds, and are not expected to give regulated exhaust emissions that differ greatly from methanol. DMF does contain a substantial amount of nitrogen, and its use could result in an increase in the number and/or concentration of several currently unregulated pollutants.

IV. DYES AND COLORANTS

Dermal contact with methanol has been shown to be one of the routes in methanol poisoning. The addition of a dye would help to deter the improper use of methanol as a degreaser or cleaning agent, during which skin contact and subsequent absorption could result. If a dye temporarily colored the skin, one would probably not use the treated methanol as a cleaning solvent. In addition, an intense or repulsive color would tend to deter the ingestion of methanol. The color should appear unpalatable even when diluted.

A. Literature Search

The cutaneous exposure of human subjects to methanol has been examined by a number of investigators. Dutkiewicz, Konczalik, and Karwacki[49] determined a mean value for the absorption rate of methanol through the skin of 0.192 mg/cm^2/min. Using this value, the researchers calculated the absorption from immersing the whole hand (440 cm^2 surface area) in methanol for twenty minutes. This immersion would result in the absorption of 1.7 mg (2 ml) of methanol. The absorption of 2 ml of methanol is approximately 5 percent of the usual fatal dose, and 33 percent of the smallest reported fatal dose (6 ml) by ingestion. Although it is unlikely that one would immerse a hand in methanol for twenty minutes without some discomfort, case studies have shown that industrial workers (painters, varnishers, hatters, etc.) have experienced blindness or even death from cutaneous exposure to methanol. Case histories of cutaneous methanol poisoning include a painter who went blind after spilling methanol on his clothes and shoes, and infants who died from a methanol soaked compress being applied to their chest or under their rubber pants.

Dutkiewicz and coworkers also determined that the rate of methanol absorption was time-dependent.[49] Table 10 illustrates the absorption rate of methanol. The absorption rate was found to consist of two phases (Figure 1). In the first phase, the absorption rate increases with longer exposure times until about 30 minutes have elapsed. The increase in absorption rate for the first phase is approximately 0.0053 mg/cm^2/min^2. The second phase shows a slight decrease in absorption rate for the remainder of the exposure time (no data available for exposures longer than 60 minutes). The overall absorption rate of methanol is considered comparable to those of benzene, xylene, and carbon disulfide.

Tada, et al,[50] conducted absorption experiments on male subjects using methanol, 10 volume percent toluene with methanol, and 50 volume percent methylchloroform with methanol. The blood methanol content was monitored during the course of the experiments at regular intervals. The work demonstrated that methanol could be rapidly absorbed through the skin, and that cutaneous absorption is a major route for methanol intake.

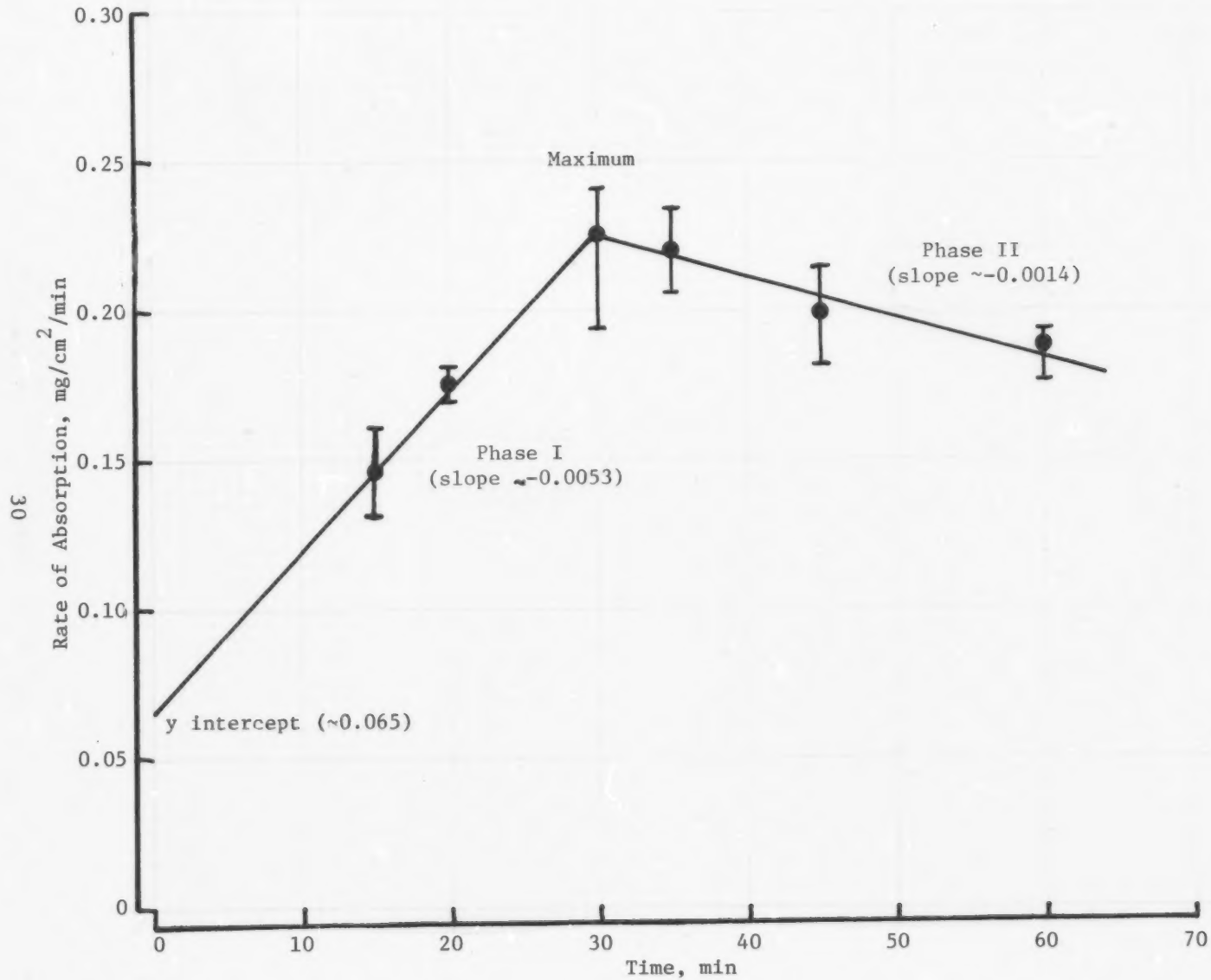

Figure 1. Experimental rate of absorption for methanol versus time[49]

TABLE 10. METHANOL ABSORPTION RATE THROUGH THE SKIN AT DIFFERENT EXPOSURE TIMES[49]

Exposure Time (min)	Number of Experiments	Range of absorbed doses, mg	Absorption Rate Through the skin ($mg/cm^2/min$)	
			Average	Range
15	3	22-27	0.146	0.131-0.161
20	3	38-40.8	0.175	0.169-0.182
30	6	65-81	0.225	0.193-0.241
35	3	81-92	0.220	0.206-0.234
45	3	92-108	0.198	0.182-0.214
60	4	119-130	0.187	0.176-0.193

Mean Value: 0.192

Ferry, Temple and McQueen[51,52] investigated the influence of combinations of methanol and petrol (gasoline) on dermal absorption. Blends of 85%, 50%, and 15% gasoline with methanol were examined. The effectiveness of barrier creams for preventing methanol absorption was also studied. After exposure, the change in skin appearance was noted for each test subject. Methanol alone caused the least dermal change, while the methanol/petrol blends caused the skin appearance to be very white and dry. It took several hours for the skin to return to its normal appearance. The methanol/gasoline blends were described by the subject as irritating and the most discomfort was caused by the 50% petrol mixture. The gasoline mixtures modified the absorption process and allowed greater amounts of methanol to be absorbed. The use of barrier creams failed to protect the skin from methanol penetration, and appeared to reduce the capacity of normal skin to resist the absorption of methanol. In another experiment, 15% methanol in gasoline was applied to a 75 cm^2 area of the forearm on two human subjects. After one minute, an increase in the sensation of heat occurred, and the experiment had to be terminated after five minutes. The skin remained inflamed for three days but did not blister. In each of these experiments, it was suggested that the absorption of methanol from a mixture with gasoline was more likely to be irritating because of the de-fatting effect caused by the petroleum distillate.

The addition of dyes has historically been used to identify a variety of fluids used in automotive applications. Table 11 presents a general list of fluids and the colors used for identification. This list includes the actual dyes used if available. A variety of alcohol-soluble dyes are commercially available in a rainbow of colors. The only colorants previously used in denaturing ethanol are methyl violet (S.D.A. 33) and iodine. Both of the colorants produce a deep blue to violet color. Commercial methanol products have typically been blue in color.[55]

TABLE 11. GENERAL AUTOMOTIVE FLUID COLORS[53,54]

Fluid	Color
Antifreeze	yellow-green blue
Automobile transmission	red
Aviation gasoline[54]	
Grade 80	red-max. 0.5 mg/gal blue[a] + max. 8.65 mg/gal red[b]
Grade 100	green-max. 4.7 mg/gal blue[a] + max. 5.9 mg/gal yellow[c]
Grade 100LL	blue-max. 5.7 mg/gal blue[a]
Brake	
DOT 3 and 4	colorless to amber
DOT 5	blue
Gasoline	orange-red green blue clear bronze
Hydraulic	green
Window washer solvent	light blue

[a] 1,4-dialkylamino-anthraquinone
[b] methyl derivatives of azobenzene-4-azo-2-naphthol (methyl derivatives of Color Index No. 26105)
[c] p-diethylaminoazobenzene (Color Index No. 11020)

B. Evaluation

The addition of a dye or colorant to identify and to deter the improper use of fluid is a common practice. The addition of a dye to temporarily stain the skin, however, is not a common practice. A methanol fuel containing a dye to stain the skin could result in irreversible coloration of clothing and vehicle components, cause excess engine wear due to deposits (although this has not been thoroughly investigated), and lead to additional exposures when trying to remove the dye from skin or clothing.

The concentration of dye in methanol needed to stain the skin is also considerably higher than the concentration of dye needed to give a distinctive color to methanol. Five methanol-soluble dyes were obtained from Pylam Products Company, Inc. for evaluation. These dyes included Pylam Bright Red, Pylam Blue, Pylam Orange, Pylam Lemon Yellow and Rhodamine B (rose color at high dilution). All five dyes gave discernable colors at a concentration of 4 mg per gallon methanol, however, only the colors for the Pylam Blue and Rhodamine B remained intense. Concentrations on the order of 400 mg of dye per gallon were needed to cause staining of the skin, but only the Pylam Blue caused a significant discoloration. For comparison, the dyes used in gasoline are present at concentrations up to 10 mg per gallon.

One company, the Lindele Corporation in Orange, California, produces two methanol fuels containing dyes. One is for a racing application (Racing Blue) and the other for street vehicles (Red fuel). Both contain proprietary additive packages, however, the dyes used in these fuels are present as a method of leak detection rather than as a stain for the skin.

A number of alcohol soluble dyes are available on the market in a rainbow of colors. While a variety of dye colors could be used for various applications, the use of a blue dye as a colorant would conform to the coloration used in commercial products containing methanol. The blue dyes also give a more intense color than other dyes at equivalent concentrations (i.e., the Pylam dyes).

If the average price for 100 pound quantities of the Pylam dyes, $19/pound (1981 price list), is used to calculate the cost impact of adding dyes to methanol, then a 4 mg/gallon dye concentration would only increase the cost of methanol 0.02¢ per gallon. This 4 mg/gallon concentration of the Pylam dyes is the amount needed to give methanol a distinctive color. If the 400 mg/gallon concentration is used for skin coloration, a 2¢ per gallon increase in the cost of methanol is calculated. The blending costs in either case would be on the order of 0.1¢/gallon if the costs for blending with methanol are comparable to those for gasoline.

The use of dyes in methanol would probably have little or no impact on the exhaust emissions, if the dyes were used at concentrations equal to or lower than those currently used in gasoline (up to 40 mg per gallon). The impact on the exhaust emissions from higher dye concentrations would depend on the chemical makeup of the dye. Dyes containing metals such as manganese (permanganate) or halogens (chlorine, bromine, iodine) should be avoided because they may damage the emission control devices and may result in exhaust emissions that could represent human health hazards.

V. EMETIC

The use of emetics as additives to methanol is another means of reducing the severity of poisoning due to its ingestion. An emetic is an agent or substance that induces vomiting, which allows the victim from an accidental or intentional ingestion of a hazardous substance to eliminate it before the body has time to absorb the poison. Posner[56] was one of the first researchers to suggest the use of an emetic as an additive to methanol. Another related group of compounds, "antialcoholics," is also a possible means of deterring the consumption of methanol.

A. Literature Search

The usefulness of emetics generally occurs after a poison has been ingested, rather than acting as a deterrent. The addition of an emetic substance should be in high enough concentration to induce vomiting even if diluted, should be reliable, and should act in a very short period of time to minimize the absorption by the body. Common practices to induce vomiting include the administration of 10 g of table salt in 200 ml of warm water (2 teaspoons in a glass of warm water[57]), the administration of 2 teaspoons of sodium bicarbonate (baking soda) in a glass of water,[32] or the administration of 30 ml (1 oz.) of syrup of ipecac to the victim.[58]

Ipecac, the emetic generally recognized by the medical profession, is obtained from the dried rhizome and root of a plant that grows in Central and South America. It consists of a variety of alkaloids which include emetine, cephaeline, emetamine, ipecacuanhic acid, psychotrine and methyl psychotrine. Ipecac is available in two forms: pure extract, and tincture. Emetine is one of the principal alkaloids of Ipecac, and it is used in Great Britain as an emetic[50] and in third world countries as an antiamebic. A list of possible emetics which would be added to methanol is included in Table 12. It should be noted that many of the substances are derived from plant tissues.

Compounds in another group (antialcoholics) are administered to individuals before injection of ethanol, and are used to treat chronic alcoholics as a means of reducing their dependency on ethanol. After the administration of antialcoholics such as disulfiram (tetramethylthiuram disulfide) or citrated calcium cyanamide, a patient experiences a number of physical responses, including vomiting, when ethanol is ingested. Disulfiram is also used in the rubber industry as an accelerator and vulcanizer, as a seed disinfectant, and as a fungicide. Since antialcoholics must be administered before the consumption of an alcohol, their use is impractical as an emetic additive to methanol.

B. Evaluation

Based on the large quantity of an emetic which would need to be added to methanol to produce the desired effect and the corresponding cost associated with this amount of emetic, the use of an emetic in methanol motor fuel would probably not be practical. About 2 ml of pure ipecac extract or about 30 ml of the syrup of ipecac (ethanol base) are required to induce vomiting.[55] A dose of 25 ml of methanol has been reported as fatal in some cases if not treated immediately; therefore, 2 ml of ipecac extract would be required for each 25

TABLE 12. THERAPEUTIC CATEGORY - EMETIC[32]

Compound	Source or Comments
Apocodeine	codeine
Apomorphine	morphine
Bayberry bark	dried root bark of Myrica cerifera L, Myricaceae
Cephaeline	alkaloid of ipecac
Citrated calcium cyanamide	antialcoholic
Disulfiram	alcohol deterrent
Dodine	agricultural fungicide
Emetine	Alkaloid of ipecac
Eupatorin	
Ipecac	root of Unagaga ipecacuanda or Uragoga acuminata
Nabam	in presence of alcohol can cause violent vomiting
Oil of Chamomile	aromatic bitter
German	volatile oil from flowers of Matricaria chamomilla L
Roman	volatile oil from flowers of Anthemis nobilis L
Sea onion	fleshy inner bulb scales of the white variety of Urginea marithima
Stillingia	root of Stillingia sylvatica L

ml of methanol fuel (8 percent). With the current cost of ipecac at $120/lb,[59] the cost impact of a methanol/ipecac fuel would be on the order of $84/gallon, a prohibitive figure. The individual alkaloid emetics that make up ipecac are even higher in cost. Emetine hydrochloride, for example, a derivative of emetine, fluctuates in price due to availability from $2200 to $2700 per pound.

The use of the relatively inexpensive materials such as table salt or sodium bicarbonate as emetics in methanol would also require excessive amounts of the additives (one half pound per gallon of methanol). These materials are only slightly soluble in alcohols and their effectiveness as emetics in alcohols is unknown. Table salt and sodium bicarbonate are not considered viable additives.

The effect of an emetic such as ipecac on the exhaust emissions from a vehicle operating on a methanol blend is unknown. Large quantities of the high molecular weight emetic would, however, likely be detrimental to the operation of spark ignited engines and possibly even to spark-assisted diesel methanol engines.

VI. ODORANTS

Another major route of methanol poisoning is inhalation. Methanol does not have a strong or distinctive odor to identify its presence, and when pure, has such a low odor intensity that one could be exposed to hazardous levels without realizing it. The addition of odorants would help identify the presence of methanol, and serve as a warning of possible hazardous conditions. A suitable odorant would need to coevaporate with methanol and be detectable at a much lower concentration than methanol vapor alone.

A. Literature Search

The Occupational Safety and Health Administration (OSHA) has set a workplace ceiling level standard of 150 ppm (200 mg/m^3) for methanol in air. Other standards for methanol exposure include the American Conference of Governmental Industrial Hygienists (ACGIH) and OSHA threshold limit value (TLV) of 200 ppm (260 mg/m^3), ACGIH short term exposure limit of 245 ppm (310 mg/m^3), and the American National Standard Institute (ANSI) ceiling concentration of 600 ppm (760 mg/m^3) and eight hour, time weighted concentration of 220 ppm (260 mg/m^3). The IDLH (Immediately Dangerous to Life or Health) value for methanol is set at 25,000 ppm, and the lower explosive limit is approximately 67,000 ppm. The values for the odor threshold have been reported to range from 100 to 2000 ppm.[23] Varying levels of impurities in methanol may account for this discrepancy; since compounds of low odor are greatly influenced by the presence of odorous impurities. If the odor threshold was at the upper end of the range, then one might not be able to detect levels where physiological effects could result.

Keller, Nakaguchi and Ware[6] screened eight substances for their effect on the odor threshold of methanol. These substances were screened initially by preparing solutions with methanol in open volumetric flasks (Table 13). The more promising of these substances in terms of cost effectiveness and odor threshold were tested further in a closed room. A measured quantity of each solution was allowed to evaporate in the room to give a 480 ppm (610 mg/m^3) concentration of methanol. The odor in the room was then evaluated by two or more individuals. The results of this second experiment are presented in Table 14. The odor threshold for reagent grade methanol used in this study was approximately 400 ppm (505 mg/m^3).

The most effective odorants tested in the study were determined to be n-butyl mercaptan and ethyl acrylate. Gasoline, giving an "old paint" odor to the blend, was not considered as effective as the others. At very low concentration levels, the odor of ethyl acrylate was described as pleasant, while at higher concentrations, the odor was found to be extremely irritating. The two mercaptans screened in the study produced very distinctive odors even at very low concentrations, however, n-butyl mercaptan was considered more unpleasant than t-butyl mercaptan. One disadvantage of using mercaptans as methanol additives is possible confusion with a natural gas leak. Natural gas also contains mercaptans as odorants. A number of other malodorous substances which could be used as odorants in methanol are listed in Table 15.

TABLE 13. ODORANT TESTS: ODOR OF VARIOUS ODORANTS ABOVE A SOLUTION IN METHANOL (In An Open Volumetric Flask)

Compound	Molarity in Methanol	Odor
Toluene	1.0	very strong
	0.1	slight
	0.01	not detectable
"Xylenes"	1.0	strong
	0.1	slight
Gasoline (estimated mol. wt. 100)	0.7[a]	strong
	0.14[b]	slight
	0.07	very slight
Ethyl acrylate	1.0×10^{-3}	strong and irritating
	1.0×10^{-4}	strong
	1.0×10^{-5}	slight and not irritating
	1.0×10^{-6}	slight and not irritating
Acrolein	0.01	slight
Crotonaldehyde	0.01	slight
n-butyl mercaptan	5.4×10^{-4}	strong and very unpleasant
t-butyl mercaptan	5.1×10^{-4}	strong and unpleasant

[a] 10 vol % or 9 wt % gasoline
[b] 2 vol % or 1.8 wt % gasoline

TABLE 14. ODORANT TESTS: EVAPORATION OF A SOLUTION IN METHANOL INTO A CLOSED ROOM[a]

Odorant	Concentration in Methanol Molarity	Approximate Concentration of Odorant in Air, ppm by Vol	Observations
Gasoline	0.4[b]	6	no noticeable odor
	1.2[c]	18	odor "like old paint," "sweet", not very alarming[d]
Ethyl acrylate	1.0×10^{-4}	0.002	odor very noticeable, distinctive, rather sweet, "like plastic"
t-butyl mercaptan	5.1×10^{-4}	0.01	odor strong, unpleasant, "like natural gas"
	1.7×10^{-4}	0.003	odor fairly strong, unpleasant, "like natural gas"
	5.1×10^{-5}	0.001	odor noticeable, unpleasant
n-butyl mercaptan	5.4×10^{-4}	0.01	odor very strong, very unpleasant
	1.8×10^{-4}	0.004	odor very strong, unpleasant
	5.4×10^{-5}	0.001	odor noticeable, more unpleasant than t-butyl mercaptan
Methanol only	--	330[e]	odor noticeable, rather sweet but irritating to nose and throat

[a]Sufficient to give 480 ppm (vol) methanol in the air
[b]5 wt % gasoline
[c]15 wt % gasoline
[d]The odor was not recognizable as that of gasoline to anyone.
[e]Methanol did not completely evaporate.

TABLE 15. MALODOROUS SUBSTANCES

Compound	Odor	Source
Aldehol	disagreeable odor	9
Acrolein	pungent odor	6
Bis(methylthio)methane	odorous principle of white truffle	9
Trans-2-butene-1-thiol	scent of skunk	60
n-butyl mercaptan	heavy skunk odor	6
sec-butyl mercaptan	heavy skunk odor	9, 61
t-butyl mercaptan	heavy skunk odor	6, 61
Crotonaldehyde	vapor extremely irritating	6
Dimercaprol	pungent offensive odor of mercaptans	9
Ethyl acrylate	acrid, pentrating odor	6
Ethyl mercaptan	penetrating leek-like odor	9
Ethyl sulfide	etheral odor	61
Gasoline	characteristic odor	6, 61
Isoamyl mercaptan	repulsive odor	9
Isoamyl sulfide		9
Isobutyl mercaptan	heavy skunk odor	6
Isobutyl sulfide		9, 61
Methyl acrylate	acid odor	9
3-methylbutanoic acid	disagreeable, rancid-cheese odor	9
3-methyl-1-butanethiol	scent of skunk	60
2-methyl-2-burtene	disagreeable odor	9
Methyl-1-(trans-2-buteryl)disulfide	scent of skunk	60

TABLE 15 (Cont.d). MALODOROUS SUBSTANCES

Compound	Odor	Source
Methyl mercaptan	odor of rotten cabbage	9
Methyl sulfide	disagreeable odor	9, 61
2-naphthyl mercaptan	disagreeable odor	9
1-octanol	penetrating, aromatic odor	9
2-octanol	aromatic, yet somewhat unpleasant odor	9
1-pentanethiol	penetrating, unpleasant odor	9
1,3 propanedithiol	disagreeable odor	9
Pyrazine	strong pyridine-like odor	9
Pyrazole	pyridine-like odor	9
2-pyrazoline	faint amine odor	9
Pyridine	characteristic disagreeable odor	9
Pynolidine	unpleasant ammonia-like odor	9
3-pynoline	unpleasant ammonia-like odor	9
Thiophene	slight aromatic odor resembling that of benzene	17
Toluene	benzene-like odor	6
Xylenes		6

B. Evaluation

Methanol's low odor intensity allows unsafe concentrations of methanol vapor to go undetected. An additive with a high odor intensity that would coevaporate with methanol should be used to indicate the presence of methanol. The use of an additive to impart an odor to methanol parallels the role of mercaptans in providing an odor to otherwise odorless natural gas.

Keller, Nakaguchi, and Ware[6] investigated a number of odorous additives for methanol. Four additives (gasoline, ethyl acrylate, n-butyl mercaptan and t-butyl mercaptan) were evaluated extensively. As mentioned previously in this report, a 15 volume percent addition of gasoline was found to produce an "old paint" odor when coevaporated with methanol. While extremely irritating at high concentrations, the odor of ethyl acrylate in methanol was determined as pleasant at very very low concentrations. The two mercaptans produced very distinctive odors even at low concentrations, with the n-butyl mercaptan being considered the more unpleasant of the two.

While the mercaptans were found to be effective odorants in Keller's work, their odor could produce confusion about the source since mercaptans are also added to natural gas. Mercaptans are also feared to be susceptible to oxidation while standing in methanol fuel for long periods of time. This oxidation process would convert the mercaptans to sulfur oxides, which have a much lower odor intensity. Organic sulfides (i.e., methyl sulfide, ethyl sulfide) have an odor slightly different from, but equivalent in intensity to, that of the mercaptans. They are also more resistant to oxidation, and would be viable alternates for odorous additives to methanol. Vehicles using methanol fuel with mercaptans or organic sulfides as odorant additives would produce exhaust emissions containing sulfur dioxide and sulfate. These exhaust emissions would be nonexistent when using pure methanol, however the levels of sulfur dioxide and sulfate emissions would be on the order of one-tenth those from the sulfur in conventional gasoline.

The use of mercaptans or organic sulfides at the levels necessary to produce a strong and unpleasant odor in methanol should not provide any problems with vehicle operation or with the health of people using the fuel blend. The use of ethyl acrylate as an odorant may not be as practical as the sulfur-containing odorants, since ethyl acrylate levels that were high enough to be detected were also irritating. This irritation of the eyes and mucous membranes could be a problem in itself. The use of unleaded gasoline as an additive was discussed in detail in Section II of this report. Bulk costs for mercaptans and organic sulfide odorants are similar, and range from $1.04 to $1.08 per pound.[61] The cost of the mercaptans or sulfides necessary to give a gallon of methanol a strong and unpleasant odor is approximately 0.05¢ (cost of 0.2 grams).

In addition to identifying the presence of methanol vapor, the use of odorants would also act as deterrents for the ingestion and for the dermal contact of methanol fuel. Prior to 1880, the only commercially available source of methanol was in the form of wood alcohol, which had a vile taste and disgusting odor. For this reason, methanol was rarely ingested or used in contact with the skin. After an inexpensive method of deodorizing wood

alcohol was introduced, methanol became a substitute for ethanol and as many as one thousand uses of poisoning were attributed to methanol between 1988 and 1913.[22] An odorant added to methanol fuel should discourage the ingestion or dermal contact of methanol fuel as did the unpleasant odor of wood alcohol.

VII. OTHER METHODS TO INCREASE SAFETY

In addition to chemical means for improving the safety of methanol, several additional methods have been proposed. They include fuel labeling, antisiphoning methods, sealed fuel handling systems and methanol education. These additional measures would help to increase the safety associated with the use of methanol as a motor fuel.

In 1976, the National Institute for Occupational Safety and Health (NIOSH) recommended standard labeling of methanol containers and areas where methanol was present.(62) The language of the warning signs is presented in Figures 2 and 3. Methanol is regulated by the Federal Hazardous Substances Act and must be labeled with "Danger," "Poison," "Cannot be made nonpoisonous," and the skull and crossbones symbol. The statement of hazard must include the language "Vapor Harmful." Wood and Buller(63) suggested labeling with "not to be taken internally" in 1904. Hagen(21), and Anderson and Nichols(8), and Wimer, Russell and Kaplan(18) have suggested similar language including the avoidance of such terms as "wood alcohol" or "methyl alcohol," since the lay person identifies the term alcohol with ethanol and deduces that it is drinkable. All references to "alcohol" should be avoided in the distribution and discussion of methanol. A term such as "fuel methanol" would be preferable.

Posner(51) has suggested the use of antisiphoning devices or techniques to remove the possibility of oral or dermal contact with fuel methanol. Very few individuals die or suffer residual effects from the ingestion of gasoline. However, the aspiration of gasoline into the lungs can cause pneumonia and sometimes even death. The ingestion or aspiration of methanol into the body is more harmful than the ingestion or aspiration of gasoline since small quantities of methanol can cause temporary or permanent blindness, and large quantities can cause death. The ingestion of methanol may also trigger abuse due to its inebriating quality. Hagen(21) suggests that strict measures must be taken to prevent oral consumption, and oral fuel siphoning should be strictly avoided.

Posner(51) has also suggested the use of sealed handling systems and redesigned fuel delivery systems. A closed system would help to eliminate dermal contact and exposure to methanol vapors. The racing organizations (CART and USAC) have been using a closed fueling system, called a "dry break" system, for many years on their racing vehicles. The system is composed of self-closing, spring-loaded valves which do not allow the fuel to flow until the union has been completed. This system, in conjunction with ground wires and fire proof clothing, helps to reduce exposure to methanol and the possibility of fire-related accidents.

Education of the general public to the dangers related to methanol would also be of great importance. Although this is probably the least cost effective method of safety enhancement, the frequency of serious accidental ingestion or exposure should be appreciably reduced. The NIOSH report(62) concludes that the safe handling of methanol depends to a great extent upon the effectiveness of employee education, intelligent supervision, and the use of safe equipment. Training programs for new and experienced employees should be conducted

METHYL ALCOHOL
(METHANOL)

WARNING FLAMMABLE

CAN BE FATAL OR CAUSE BLINDNESS IF SWALLOWED

Keep away from heat, sparks, and open flame.
No smoking permitted.
Do not take internally.
Keep container closed.
Avoid prolonged or repeated breathing of vapor or contact with skin.
Avoid contact with eyes.
Use with adequate ventilation.

First Aid: In case of eye or skin contact, flush thoroughly with copious amounts of water. In case of accidental swallowing, call a physician and induce vomiting if the patient is conscious. Change clothing if contaminated.

In case of:

Fire: Use water, spray, "alcohol" type foam, dry chemical, or carbon dioxide extinguishers.

Spill: Flush area with water spray.

Figure 2 . Warning sign for storage tanks and containers(62)

METHYL ALCOHOL
(METHANOL)

WARNING FLAMMABLE

HARMFUL IF INHALED
CAN BE FATAL OR CAUSE BLINDNESS IF SWALLOWED
IRRITATING TO SKIN OR EYES

No smoking permitted.
Provide adequate ventilation.

Figure 3 . Warning sign for areas in which methyl alcohol is present(62)

periodically. There have been documented cases in which methanol has been used in an infant's formula (mistaken for water), applied to the skin with methanol-soaked compresses on the chest or under babies' rubber pants, spilled on clothing of workers, and abused in every form from antifreeze to solvents to alcohol fuel (Sterno). Although education is not the complete answer, it would help to reduce many of the accidental hazards involved with methanol.

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APPENDIX A

BACKGROUND AND HISTORY

Methanol is the simplest of alcohols. Synonyms include methyl alcohol, wood alcohol, wood spirit, carbinol, methylated spirit, Columbia spirit, colonial spirit, odiophorous spirit, pyroxylic spirit, methylol, monohydroxymethane, and methyl hydroxide. Methanol is a flammable, toxic liquid which burns with a non-luminous, bluish flame. It has a slight "alcohol" odor when pure, but the crude material may have a repulsive, pungent odor. It is miscible with water, ethanol, ether, benzene, ketones and most other organic solvents; is usually a better solvent than ethanol; and forms azeotropes with a number of compounds. Methanol is used as an industrial solvent, an ingredient in antifreeze, a denaturant for ethanol, a fuel for picnic stoves and soldering torches, an extractant for animal and vegetable oils, a softening agent for pyroxylin plastics and many other applications. The chemical and physical properties of methanol are listed in Table A-1.

Methanol can be produced from raw material sources that can be burned to produce CO and H_2 (synthesis gases). The sources of methanol include non-renewable ones such as coal, natural gas, petroleum, and oil shale as well as renewable sources such as municipal trash, agricultural and animal wastes, and wood and wood waste. The destructive distillation of wood as a method of production for methanol has completely disappeared in the United States, although some methanol is made commercially as a by-product in the production of charcoal. The conversion of natural gas to methanol is currently the major source. Gasification of coal and the pyrolysis of waste have become much more popular, however. Recently, work has begun by a group of microbiologists in England to grow bacteria capable of converting methane to methanol.(1)

The original production of alcohols is lost in antiquity. Evidence of fermentation has been found depicted on Mesopotamian pottery dated circa 4200 B.C. A wooden model of an Egyptian brewery dated circa 2000 B.C. has also been found. In 1661, Boyle discovered a volatile compound in products from the dry distillation of hardwood which he named "odiophorus spirit." This crude form of methanol was later referred to as wood alcohol. Methanol was confused with the fermentation product, ethanol, for over a century and a half until its chemical structure was determined by Dumas and Peligot in 1831.(2)

In about 1830, alcohol became a popular fuel for lighting, replacing the malodorous fish and whale oil. By the middle of the nineteenth century, methanol was widely used in France as a heating, lighting, and cooking fuel. By the 1880's, kerosene had replaced methanol as a lighting fuel because of its more luminous flame.(3)

The use of alcohol (ethanol) as a fuel for internal combustion engines was first attempted in Germany at the turn of the century. Alcohol was found to be impractical as a fuel for engines of that era since most of them were single-cylinder and had a low-compression ratio (3 or 4 to 1). Mixing of alcohol and gasoline was not considered because the commercially produced alcohol of that

TABLE A-1. PROPERTIES OF METHANOL(1,2)

Property	Value
Formula	CH_3OH
Molecular Weight	32.042
Carbon to Hydrogen Weight Ratio	3.0
Carbon, % by Weight	37.5
Hydrogen, % by Weight	12.5
Oxygen, % by Weight	50.0
Autoignition temperature, °C	385
Boiling Point at 760 mm HG, °C	64.51
Critical Pressure, Atmospheres	78.5
Critical Temperature, °C	240.0
Dielectric Constant at 20°C	31.2
Dielectric Constant at 25°C	32.6
Dipole Moment at 25°C Debye Units	1.66
Electrical Conductivity, at 25°C ohm-1/cm	1.5×10^{-9}
Flammability Limits, in air, Vol. %	
Lower Limit (at 25°C)	6.7
Upper Limit (at 60°C)	36.0
Flashpoint (ASTM Tag Open Cup), °C	15.6
Freezing Point, °C	-97.49
Heat of Combustion, gross, of liquid at 25°C cal/mole	173,650
Heat of Combustion of liquid at 20°C kcal/moke	170.9
Heat of Vaporization at bp & 1 atm Cal/mole	8430
Heat of Vaporization at bp & 1 atm, cal/g	262.8

TABLE A-1 (Cont'd). PROPERTIES OF METHANOL(1,2)

Property	Value
Heat of Formation at 25°C, cal/mole	
of liquid	57,036
of vapor	48,100
Heat of Fusion at -97.8°C cal/g	22.0
Ignition Temp, in Air (atm, Pressure),°C	385
Ignition Temp. (apparent), in Air, °C	470.0
Melting Point, °C	-97.8
Refractive Index, n 20/D	1.3286
Specific Conductivity at 25°C	1.5 x 10-9 mhos/cm
Specific Gravity at 20/4°C	0.7915
Specific Heat, Liquid, cal/g	
0-3°C	0.565-0.575
5-10°C	0.579-0.587
15-20°C	0.594-0.600
25-30°C	0.605-0.609
35-40°C	0.613-0.616
Surface Tensions, dynes/cm	
at 15°C	22.99
at 20°C	22.55
at 30°C	21.69
Vapor Density (air = 1)	1.11
Vapor Pressure, mm Hg	
at 0°C	29
at 10°C	52
at 20°C	96
at 30°C	159
at 40°C	258
at 50°C	410
at 60°C	630
at 64.5°C	760
Viscosity, cP	
at 15°C	0.6405
at 20°C	0.5945
at 25°C	0.5525
at 30°C	0.5124

time period had a water content of not less than 5 to 6%, rendering it immisable with gasoline.[4]

With the advent of World War I, interest in alcohol as a fuel was revived in Germany, which faced serious petroleum shortages. Alcohol mixed with benzene and available gasoline was used as fuel for German airplanes, Zeppelins, and ground transportation, as well as to manufacture explosives and other war materials. In Sweden, the only fuel available was a mixture of alcohol, benzene, acetone, and turpentine. After World War I, legislation was enacted by Austria, Brazil, Czechoslovakia, France, Germany, Hungary, Italy, Yugoslavia, Latvia, Poland, Spain, and Sweden to enforce the use of ethanol as a motor fuel. Even in the United States, which had a surplus production of petroleum relative to domestic requirements, the farming community pushed for legislation (the 1906 Industrial Denatured Alcohol Act) to enforce the use of ethanol/gasoline mixtures aided by tax exemptions. In the United Kingdom and Australia, ethanol fuels were marketed without Government compulsion.[4]

Just before and during the second world war, petroleum was again in short supply. A relatively small number of vehicles were operated on the fumes from burning wood. These fumes contained carbon moxoxide, methane, and hydrogen as well as some methanol. About 9000 passenger buses, trucks, pleasure cars, and even two taxi cabs used wood as a fuel source. The majority of the wood burning vehicles were operated in France (4500), Germany (2200), and Italy (2200). Wood filling stations began to dot the countryside in these countries, and wood was sold in bundles of 30 to 60 pounds.[5]

Following World War II, a promotional effort was undertaken to use water-alcohol injection in spark-ignited automobile and truck engines. Since that time, methanol has been used in all types of engines ranging from aircraft engines to racing vehicles. More recently, interest in methanol as a fuel resulted from the possible reduction of exhaust emissions, independence from foreign oil supplies, and utilization of domestic surpluses of biomass.[6]

The toxicity of methanol in an industrial environment was first noted by MacFarlan[7] in 1855, among cabinet workers, metal workers, and hatters who used wood naphtha and methylated spirits. Prior to 1880, the only commercial source of methanol was from the destructive distillation of wood and poisioning from methanol was virtually unknown. Wood alcohol, the product from the destructive distillation of wood, had a vile taste and disgusting odor and was rarely ingested. In the 1890's, a relatively inexpensive method of deodorizing wood alcohol was introduced. The resulting products were packaged under various names such as Columbia Spirits, Purified Wood Alcohol, and Colonial Spirits and were advertized as a substitute for ethanol. Uses included the manufacture of varnishes, liniments, tinctures, hair dyes, fuels for lamps and stoves, toilet articles, perfumes, alcoholic extracts, cheap whisky and patent medicines. Not until 1923, when a group of dock workers in Germany were poisoned by ingestion, did the public finally realized that methanol really was a poison. During World War II, it was estimated that about six percent of the nonfatal cases of blindness to servicemen were caused by methanol.[2]

Even today methanol poisoning is not uncommon. Methanol is purchased in many forms and used as a substitute for ethanol in order to enhance the

intoxicating effects. Methanol has also been mistaken for water in infants formula and for ethanol or rubbing alcohol in chest compresses. A number of infants have died from prolonged skin contact to methanol applied under rubber pants. These cases and many others reflect the ignorance of the public to the toxic effects of methanol.

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